Gulf Coast Aerosol Research and Characterization Program (Houston Supersite)

PROGRESS REPORT

EPA Contract No. R-82806201

between the Environmental Protection Agency and the
University of Texas at Austin

Submitted by:

Dr. David Allen
(allen@che.utexas.edu)
512-471-0049

Center for Energy and Environmental Resources
The University of Texas at Austin
10100 Burnet Road, Bldg. 133
MS R7100
Austin, Texas 78758

Quarterly progress report for October, 2001

Date of Report: February 27, 2002

EPA Agreement No.: R-82806201

Title: Gulf Coast Aerosol Research and Characterization Study

Investigators: Dr. David Allen (PI) and Dr. Matthew Fraser (Co-PI)

Institutions: University of Texas and Rice University

Research Category: Air Quality/Fine Particulate Matter

Project Period: 01/15/00-11/30/03

Objective of Research: Characterize fine particulate matter and fine particulate matter formation processes in Southeast Texas

Progress Summary/Accomplishments:
During the final quarter of 2000, the intensive sampling period for the Houston Supersite was conducted, in coordination with an air quality study focussed on gas phase chemistry (the Texas Air Quality Study). Data analyses, focussed on the selection of potential modeling episodes during the intensive period, are presented in this report.

Overview

During the final quarter of 2000, the intensive sampling period for the Houston Supersite was conducted, in coordination with an air quality study focussed on gas phase chemistry (the Texas Air Quality Study, TexAQS). Data analyses, focussed on the selection of potential modeling episodes during the intensive period, are presented in this report. Specifically, data from the real time measurements of fine particulate matter mass, inorganic ion concentrations (24 hour samples), organic and elemental carbon concentrations (24 hour samples) and organic functional groups (24 hour samples) are presented.

Sampling Locations

Inorganic ion concentrations, organic carbon concentrations, elemental carbon concentrations and total aerosol mass (Federal Reference Method, FRM) were measured daily at 8 sites during the intensive sampling period of the Houston Supersite. The sampling locations were:

- Aldine (north-central Houston, urban receptor site)
- Bayland Park (west Houston, urban receptor site)
- Channelview (east Houston, industrial source region)
- Conroe (rural site, northwest of Houston)
- Deer Park (east Houston, industrial/residential source region)
- Galveston (coastal site southeast of Houston)
- Hamshire (rural site east of Houston)
- HRM 3 (east Houston, industrial source region)

As shown in the map given in Figure 1, these locations represent a distribution of locations, and, as noted above, the sites represent a distribution of rural, industrial source region and urban receptor sites.

Real time (TEOM) measurements of fine particulate matter mass were made at five of the eight sites listed above, plus one additional site:

- Channelview (east Houston, industrial source region)
- Conroe (rural site, northwest of Houston)
- Deer Park (east Houston, industrial/residential source region)
- Galveston (coastal site southeast of Houston)
- Hamshire (rural site east of Houston)
- Mae Drive, also known as Houston East (east Houston, industrial/residential source region)

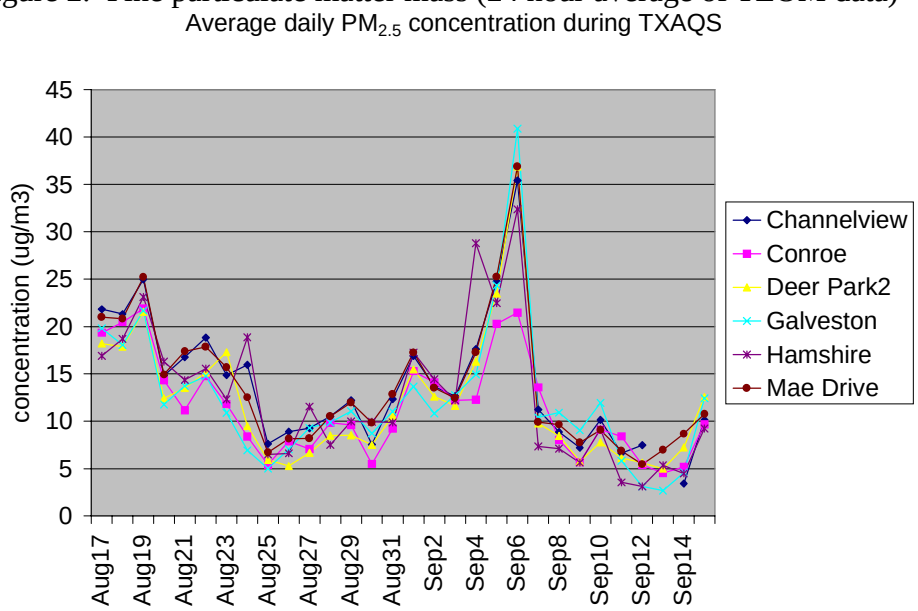
In addition, organic functional groups were measured at the Aldine, HRM3 and LaPorte (adjacent to Deer Park) sites. These measurements were made using a low pressure impactor/infrared microscopy method described in a previous quarterly report.

Figure 1. Map of southeast Texas showing the Houston metropolitan area (in white) and the sampling sites operated during the Houston Supersite intensive sampling period.

The data in this report will examine the spatial and temporal variability in fine particulate matter mass and compositions, with the goal of identifying candidate modeling episodes for the intensive period.

Figure 2 reports the daily average fine particulate matter mass for the period August 17 – September 15, 2000.

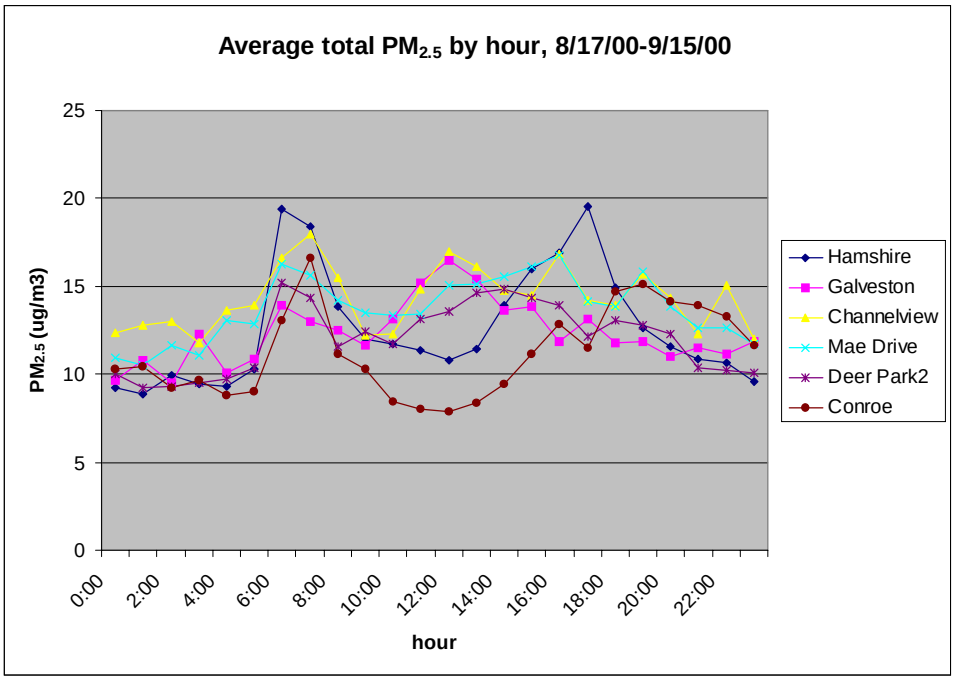
Figure 2. Fine particulate matter mass (24 hour average of TEOM data)



Several distinct periods emerge in the data set. The period from August 17-24 exhibits moderate, but steadily decreasing fine PM concentrations. Concentrations are relatively uniform throughout the region. The period from August 25-31 exhibits low, but slightly increasing total mass concentrations that are also relatively uniform throughout the region. The period from September 1-6 exhibits the highest concentrations. During this period, widespread regional fires were occurring upwind of the sampling region. Finally, during September 7-15, total mass concentrations returned to relatively low levels.

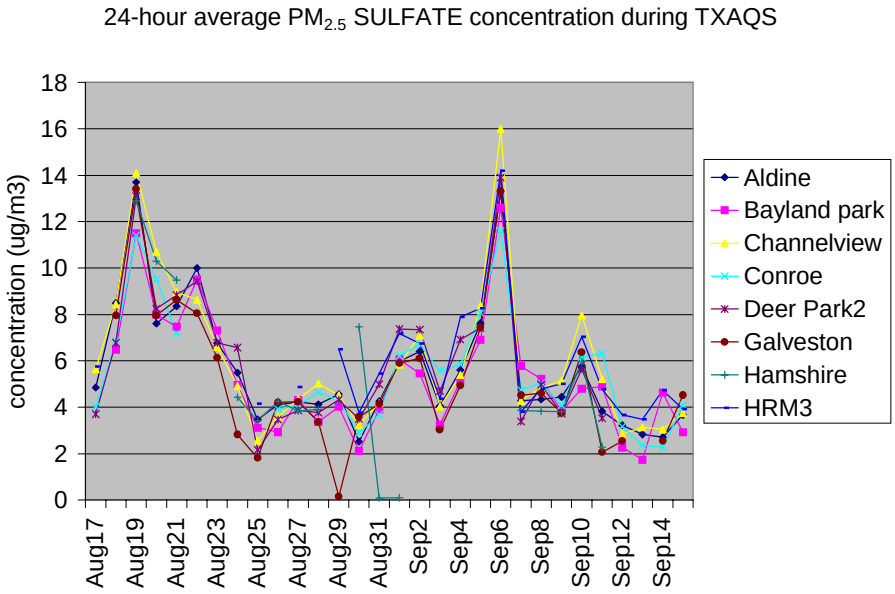
Figure 3 shows the time of day variation in these fine PM total mass concentrations during the same period. Some of the rural sites (Hampshire, Conroe) exhibit morning and afternoon peaks, while some of the industrial sites (Channelview, Mae Drive) show a weak mid - day peak. PM composition data can lend more insight into these trends.

Figure 3. Fine particulate matter mass (1 hour average of TEOM data). The data collected at each hour of the day were averaged over the days between 8/17 and 9/15/2000.



The dominant component of fine PM mass in the Houston area is sulfate. Figure 4 shows the daily average concentrations of sulfate ions at the sites where speciation measurements were made.

Figure 4. Sulfate concentrations (24 hour averaged FRM samples) during the intensive sampling period.

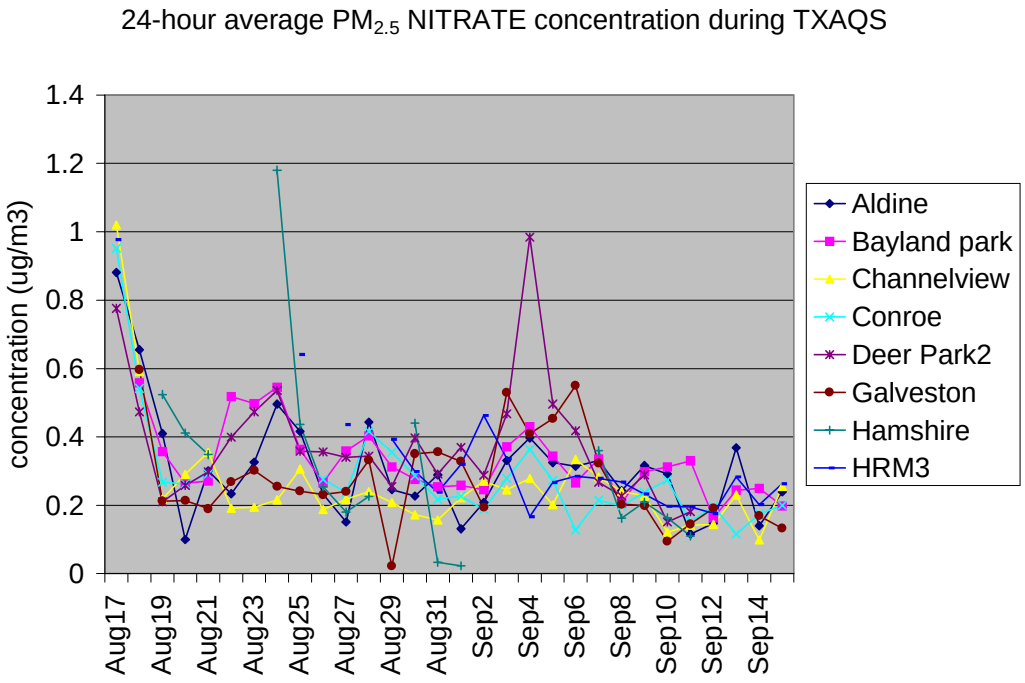


Again, several distinct periods emerge in the data set. The period from August 17-24 exhibits moderate, but steadily decreasing fine PM sulfate concentrations. Concentrations are relatively uniform throughout the region. The period from August 25-31 exhibits low sulfate concentrations (like total mass), but the concentrations exhibit some spatial variability (unlike total mass). The period from September 1-6 exhibits the highest concentrations. During this period, widespread regional fires were occurring upwind of the sampling region, and the high sulfate concentrations observed during this period may be indicative of heterogeneous chemistry increasing the rate of SO_2 oxidation. Finally, during September 7-15, sulfate concentrations returned to relatively low levels (like total mass), except for September 10, which saw a region-wide increase in sulfate mass (much weaker increase for total mass).

Inorganic nitrate (as measured in samples collected over 24 hours on filters) is a relatively minor component of fine PM mass in the Houston area. Other nitrate measurements (near real time flash volatilization measurements) confirm that, on average, nitrate is a minor component of Houston fine PM, but these near real time measurements also suggest that transient high nitrate concentrations are observed. These near real time measurements will be discussed in more detail once they have been through quality assurance checks.

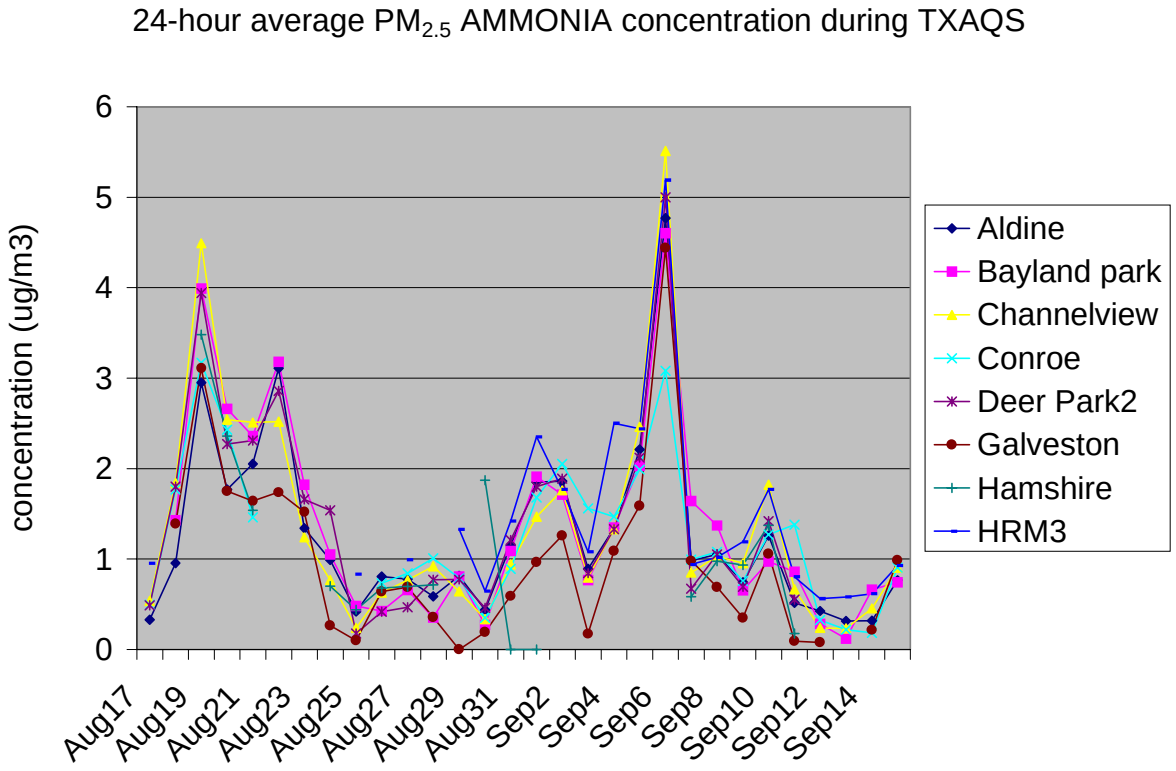
Figure 5 shows the daily average concentrations of nitrate ions at the sites where speciation measurements were made. Even in the 24 hour average data, sporadic increases in concentrations are observed at both rural (Hamshire) and industrial (Deer Park) sites.

Figure 5. Nitrate concentrations (24 hour averaged FRM samples) during the intensive sampling period.



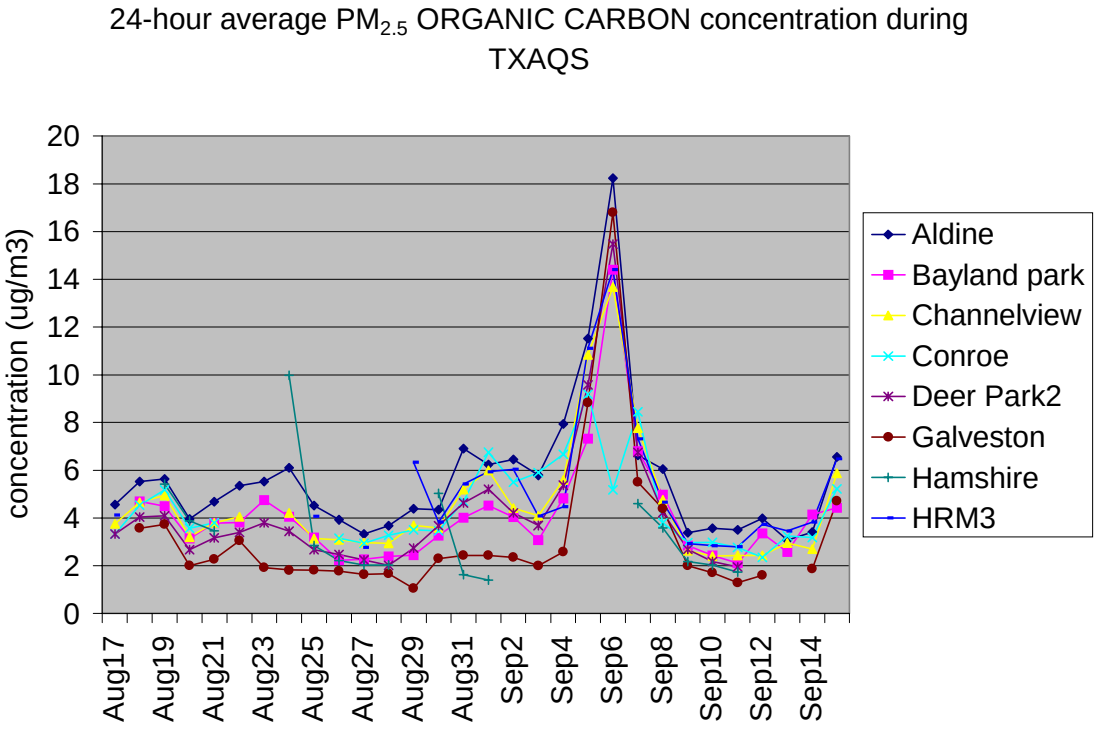
Ammonium concentrations are a significant component of fine PM mass in the Houston area and in the 24 hour samples, generally track sulfate concentrations. Other ammonium measurements (near real time PILS measurements) suggest that at times, the molar ratio of particulate ammonium to total anion concentrations can significantly exceed 1 (values in excess of 2). This excess ammonium is not apparent in the 24 hour average data, however. The near real time PILS measurements will be discussed in more detail once they have been through quality assurance checks.

Figure 6. Ammonium concentrations (24 hour averaged FRM samples) during the intensive sampling period.



Organic carbon can be a significant component of fine particulate matter in Houston, however, the contribution, as shown in Figure 7 can be episodic in nature. Several distinct periods of organic carbon concentrations emerge in the data set. The period from August 17-31 exhibits moderate, relatively constant and relatively uniform concentrations (when concentrations are averaged over 24 hours). This contrasts somewhat with the sulfate and total mass concentrations, which had higher concentrations in the first week of this two week period than in the second week. The period from September 1-6 exhibits the highest concentrations (like sulfate and total mass). Again, during this period, widespread regional fires were occurring upwind of the sampling region, and the high organic carbon concentrations are likely due to these fires. Measurements of the concentrations of organic molecular markers of cellulose combustion will be made for this period. These measurements should help refine the contribution of fires to the fine particulate matter concentrations during this period, however, these measurements are not yet available. Finally, during September 7-15, organic carbon concentrations returned to relatively low levels (like total mass).

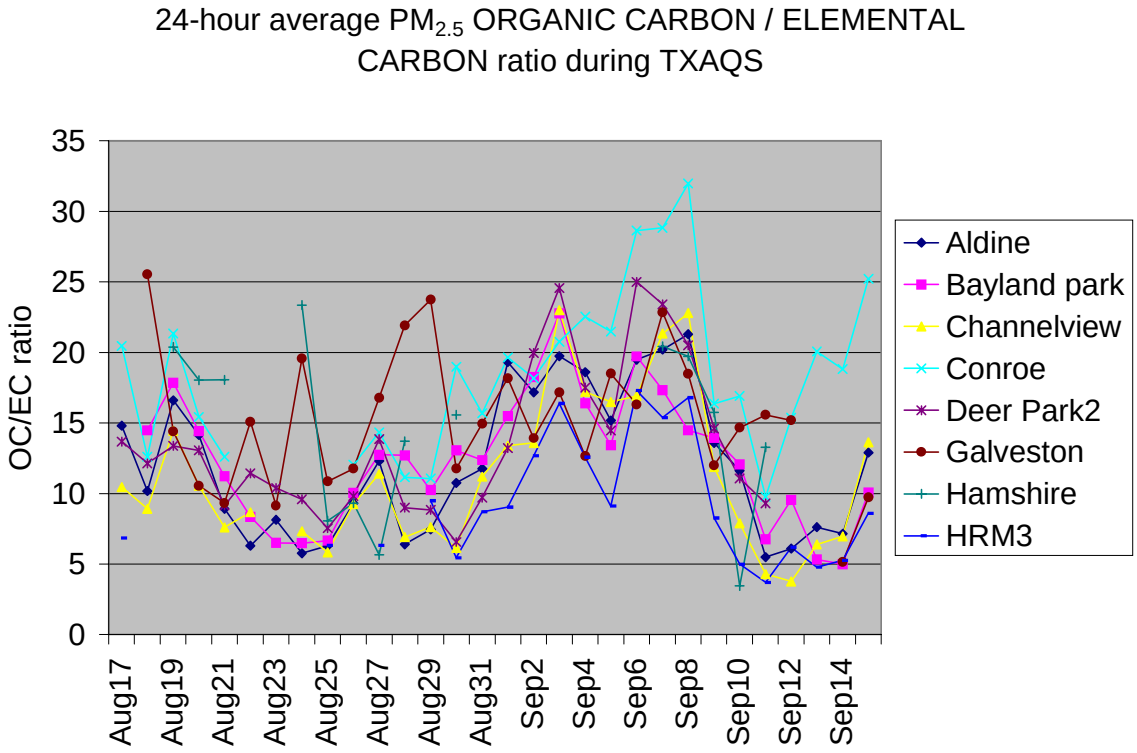
Figure 7. Organic carbon concentrations (24 hour averaged FRM samples) during the intensive sampling period.



While elemental carbon is generally not a significant component of fine particulate matter in Houston, the ratio of organic carbon (OC) to elemental carbon (EC) is an indicator of the ratio of secondary to primary organic carbon. Typical ratios of OC to EC observed in primary urban aerosol are less than 3, therefore, values significantly in excess of 3 indicate substantial secondary organic aerosol formation. As shown in Figure 8, the OC/EC ratios observed in Houston are above 5 for virtually the entire intensive period, for virtually all sites, suggesting that secondary organic aerosol is a significant component of fine particulate matter mass over a broad area.

Again, several distinct periods of organic carbon to elemental carbon ratios emerge in the data set. The period from August 17-31 exhibits OC/EC ratios ranging mainly from 5 to 20, with fairly extensive variability between sites. The period from September 1-6 exhibits the highest ratios (like organic carbon). Again, during this period, widespread regional fires were occurring upwind of the sampling region, and the high organic carbon to elemental carbon ratios may be due to these fires, although some elemental carbon would be expected in the emissions from these fires. An alternative hypothesis is that the additional carbonaceous aerosol mass causes, through a larger aerosol phase volume, more semivolatile material to partition into the aerosol phase. Finally, during September 7-15, the ratios returned to relatively low levels (like OC), except for the Conroe site.

Figure 8. Organic carbon/Elemental carbon ratios (24 hour averaged FRM samples) during the intensive sampling period.



Relatively high concentrations of secondary organic aerosol, as suggested by Figure 8, should also be indicated by the presence of carbonyl and organonitrate functional groups in the organic aerosol. Figures 9 and 10 show time series for carbonyl and organonitrate functional groups at three sites for the intensive period. Two features are worthy of note in these data. First, the median absorbance areas per cubic meter of sampled air are comparable to values measured during photochemical episodes in Los Angeles, where secondary organic aerosol is a major contributor to particulate matter mass. This supports the data in Figure 8, which suggests the importance of secondary organic aerosol. In addition, Figures 9 and 10 show that on certain days, very high concentrations of carbonyl and organonitrate groups are observed (suggesting very fast secondary organic aerosol formation?).

Figure 9. Carbonyl carbon concentrations (generally 24 hour averaged impactor samples) during the intensive sampling period.

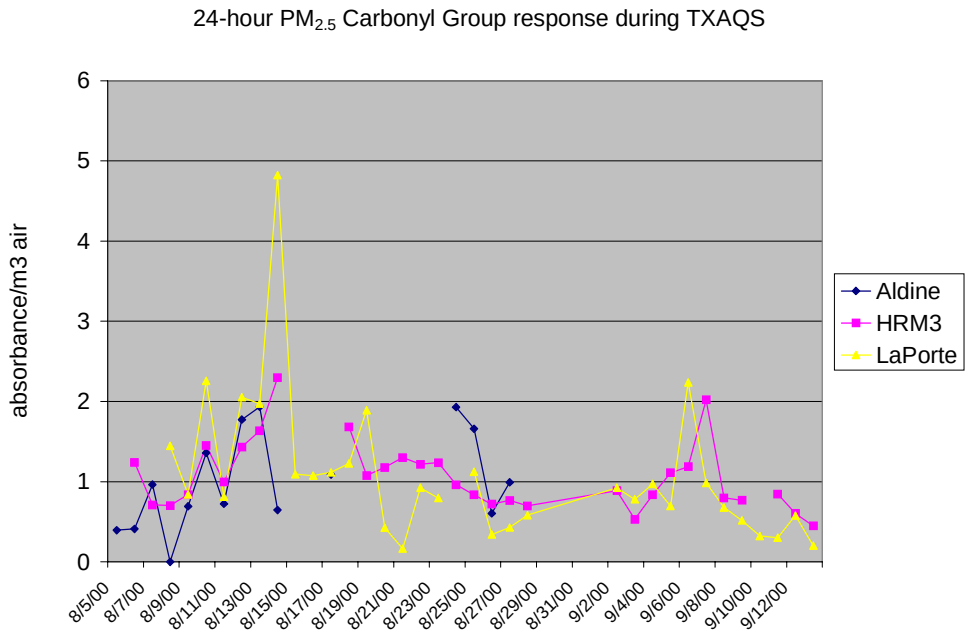
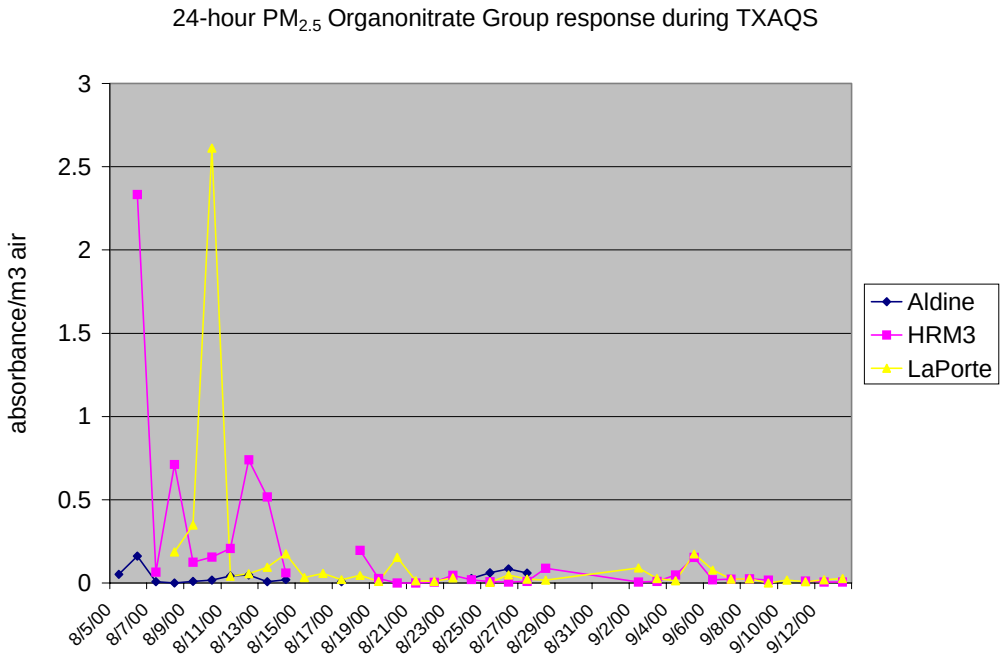
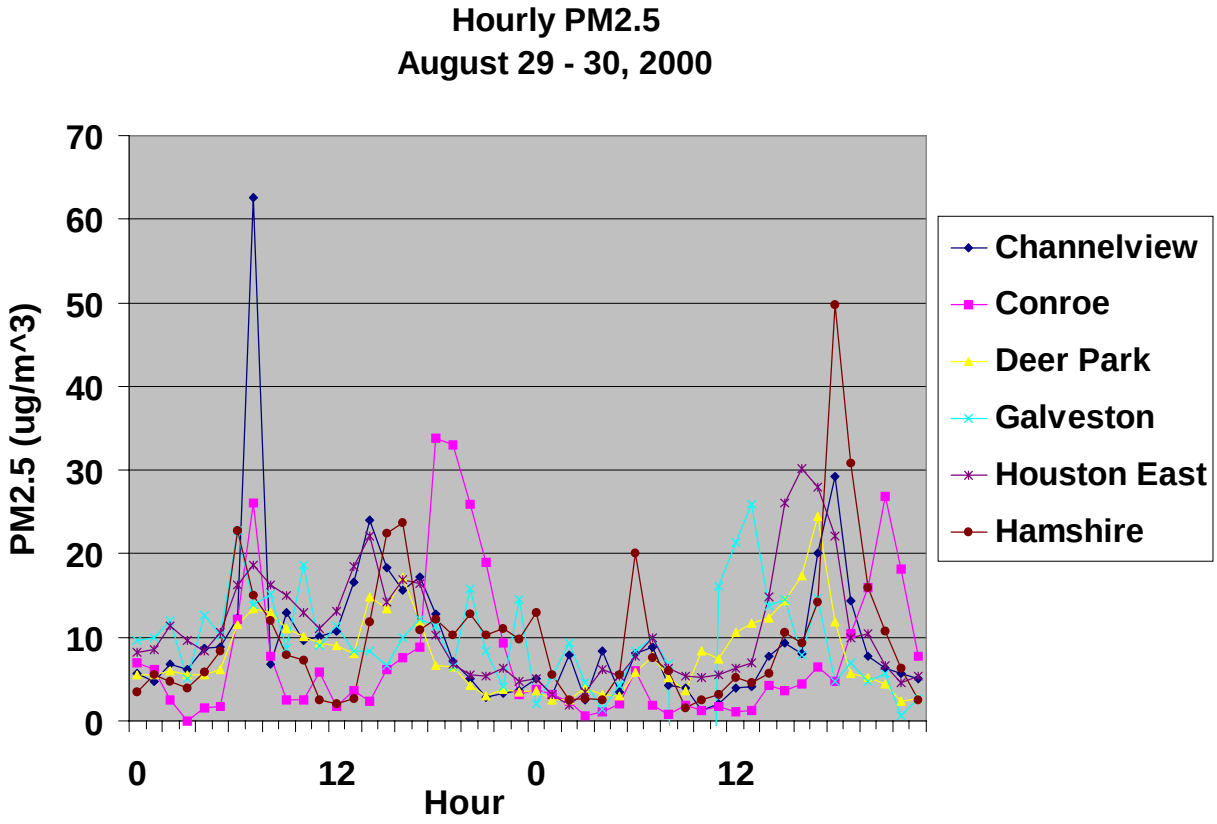


Figure 10. Organonitrate concentrations (generally 24 hour averaged impactor samples) during the intensive sampling period.



The data presented in Figure 2 and Figures 3-10 are generally 24 hour average data, and as noted in the discussion of several of the aerosol components, the finer time resolution data indicate that concentrations of most species show substantial variability over a 24 hour period. Subsequent quarterly reports will address this issue, however this will not be discussed in detail here until the underlying data undergo quality assurance checks. Nevertheless, data from TEOM measurements, which have been quality assured, give some indication of the variability to be expected. Figure 11 shows time series for fine particulate matter mass during on August 29-30. As noted above, this was a day with moderate particulate matter concentrations, but ozone concentrations in the region were high, exceeding 200 ppb.

Figure 11. Time series of fine particulate matter concentrations show substantial spatial and temporal variability, even though 24 hour average data are relatively uniform



Recommendations for modeling episodes

Three distinct modeling episodes emerge from a preliminary analysis of the fine particulate matter data from the Houston Supersite intensive, held from mid-August to mid-September, 2000.

1. August 17-24 exhibits moderate, but steadily decreasing fine PM concentrations, dominated by sulfate with evidence of significant secondary organic aerosol formation. Total mass concentrations, averaged over 24 hours are relatively uniform throughout the region and gas phase photochemistry was moderate.
2. August 25-31 exhibits low, but slightly increasing total mass concentrations over the episode that are also relatively spatially uniform (when averaged over 24 hours) throughout the region. This was a period of intense photochemical activity in the Houston area. This episode is of particular interest because in many regions, ozone and fine particulate matter concentrations are highly correlated. This episode provides a counter-example.
3. September 1-6 exhibits the highest concentrations of fine particulate matter observed during the intensive sampling period, due to widespread regional fires. There is some evidence of heterogeneous chemistry.

The September 7-15 period will likely not be of interest for modeling because of the low concentrations of fine particulate matter and because many of the supporting measurements (such as aircraft data), were not collected during this period.